

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Antioxidant Compositions

We, WINGFOOT CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, with offices at 1144 East Market Street, Akron, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preservation of rubber, and more particularly to the provision and use of a new class of nonstaining or nondiscoloring age resistors for rubber.

Rubber is subject to deterioration from many sources, such as sunlight, ozone, atmospheric oxygen, presence of heavy metals, etc. Both cured and uncured natural and synthetic elastomers are subject to deterioration. Deterioration in cured stock may likewise vary with the type of stock, the state of cure, the amount of surface exposed and the temperature at which the rubber is being used. An ideal antioxidant would be one which would protect rubber from deterioration regardless of kind, in the cured or uncured state, no matter where used. Since no such antioxidant has been discovered, compromises must be made in the selection of an antioxidant for use in rubber.

With the increasing demand for white or light-colored rubber articles there arose a need for antioxidants which would not discolor rubber or stain objects in contact with rubber. The older antioxidants produced very bad discoloration and staining. Certain alkylated phenols have been found to be antioxidants which produce little discoloration or staining. While many phenols have some antioxidant activity, there is a great difference between various phenols as to their effectiveness and also as to their degree of discoloration of rubber goods.

The effectiveness of a phenolic antioxidant will vary with the degree of alkylation, the type of alkyl groups present and the location of the substituent alkyl groups. Furthermore, the vapor pressure of the phenolic molecule

is of particular importance for certain uses, i.e. for high temperature uses and for uses wherein large rubber surfaces are exposed. Again compromises may have to be made, for example, a good antioxidant may be too volatile for general usage while, on the other hand, a nonvolatile material may be a poor antioxidant.

According to the present invention, a class of phenols has been discovered which exhibit unusual and unexpected antioxidant activity, and which are relatively nonvolatile. They exhibit a high degree of protection for rubber against sunchecking and against atmospheric oxygen, produce little or no discoloration in rubber, and are also nonstaining. Furthermore, they are derived from cheap raw materials and hence possess an economic advantage over most antioxidants of this general class.

The customary phenolic antioxidant is quite volatile because of the difficulty of effecting heavy alkylation, most phenolic antioxidants being cresol derivatives. Now, it has been found that, by selecting the alkyl substituents carefully and by reacting them with phenol in a stepwise order, a class of antioxidants may be produced easily and economically which has low volatility and which displays excellent antioxidant properties. The age resistors of this invention which can be produced in this manner, are phenols having at least three tertiary alkyl radicals attached to the ring, at least one of the radicals being selected from the group consisting of tertiary octyl and tertiary nonyl radicals and at least one being selected from the group consisting of tertiary butyl and tertiary amyl radicals.

In the practice of this invention, the alkylated phenolic compounds can be made by reacting phenol with an olefin selected from the group consisting of tertiary octenes and tertiary nonenes and then with another olefin selected from the group consisting of isobutylene and tertiary amylenes. Mixtures of octenes and/or nonenes and mixtures of isobutylene and/or amylenes can be used, if desired.

Many alkylated phenols have not proved to

[Price 3s. 0d.]

be good antioxidants. This may be due to the fact that the action of the OH group must be inhibited in order to have a good antioxidant. For this purpose large groups ortho to the hydroxyl are desirable. The size of these groups is limited, however, by the fact that heavy chains are not easily attached and by the fact that the composition would become too costly and difficult to make to use as an antioxidant if the chains were too large.

By the practice of this invention, the maximum effect is obtained by securing tritertiary substitution of the phenol nucleus with octyl, nonyl, butyl or amyl groups. In order to obtain the desired antioxidants the heavier tertiary olefin is reacted with phenol first and thereafter the product of that reaction is reacted with the lighter tertiary olefin.

While the invention includes the isolation and use of the individual compounds, the composite reaction products are preferred as age resistors, since their use saves the additional costs of purification or separation. The products may be produced from pure compounds or from mixtures of compounds.

For best results the reaction temperature during alkylation will ordinarily be maintained within a range of 50° C. to 150° C. If the temperature is too high, the alkylation catalyst may become a catalyst for dealkylation. During the second stage of the alkylation process, it is often desirable to maintain the temperature below 90° C in order to prevent dealkylation and in order to obtain more complete alkylation. The temperature will of course vary with variations in customary reaction conditions such as, for example, pressure, catalyst used, etc.

In the practice of the invention, one or more of the customary acidic alkylation catalysts is used to activate and accelerate the reactions. For example, sulfuric acid, benzene sulfonic acid, toluene sulfonic acid, activated clays, stannic chloride, ferrous chloride, boron trifluoride, zinc chloride, the ferrous and ferric halides, the stannous and stannic halides, aluminum halide and aluminum oxide will catalyze the reactions. Usually, concentrated sulfuric acid is used as the alkylation catalyst. The catalyst will ordinarily be used in an amount of at least 0.5% of the total weight of reactants, i.e., phenol plus olefins, but larger amounts of catalyst, for example, up to 5.0% by weight of the reactants, are also satisfactory.

By the process of the invention a phenolic antioxidant can be obtained which is substantially trialkylated with tertiary alkyl radicals. In order to obtain the desired alkylation, the phenol must be reacted with the tertiary octene or tertiary nonene as the first step in the process, the use of at least one mol. of tertiary octene or tertiary nonene per mol of phenol being necessary in order to obtain at least monoalkylation of a substantial portion

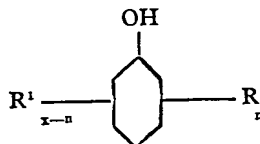
of the phenol molecules. When only one mol of tertiary octene or tertiary nonene is used in the first step, it becomes necessary to use at least two mols of a tertiary butene or a tertiary pentene in the second step in order to obtain the desired trialkylation. It is preferred to use more than one mol of the tertiary octene or tertiary nonene per mol of phenol in the first step of the process because it is desirable to obtain phenolic reaction products having more than one position on the phenolic ring substituted with the heavier alkyl radicals. Still more preferred is the use of at least two mols of the tertiary octene or nonene. More than two mols of tertiary octene or tertiary nonene per mol of phenol can be used in the first step in order to insure that a substantial portion of the phenolic reaction products will be dialkylated with tertiary octyl or tertiary nonyl radicals. At least one mol of isobutylene and/or tertiary amylene must be used and the total amount of olefin must be at least three mols per mol of phenol.

It is possible to obtain a phenolic antioxidant reaction product in which a major portion of the phenolic molecules will be dialkylated with either a tertiary octyl or a tertiary nonyl group and monoalkylated with either a tertiary butyl or a tertiary amyl group. Because of chemical selectivity, one tertiary octyl or tertiary nonyl group will normally attach to the position para to the hydroxyl and the other ortho to the hydroxyl. This would leave the other ortho position available for a tertiary butyl or tertiary amyl group. If sufficient octylene or nonylene is not used for substantially complete dialkylation, the tertiary octyl or tertiary nonyl radical will attach to the para position, leaving the two ortho positions available for the tertiary butyl or tertiary amyl groups. These two types of compounds account for a substantial portion of the reaction product, i.e. at least 60% of the total composition, and under proper reaction conditions will amount to about 85% to 95% of the total composition. Other compounds which can be present in the reaction product in varying but minor amounts are (1) the disubstituted phenols in which both substituents are di-tertiary octyl (or nonyl) or di-tertiary butyl (or amyl) or in which one substituent is tertiary octyl (or nonyl) and the other substituent is tertiary butyl (or amyl) and (2) the trisubstituted phenols in which all three substituents are tertiary octyl (or nonyl) on the one hand or tertiary butyl (or amyl) on the other.

Preferably, an excess of the heavier olefin is used, i.e., more than two mols of olefin for each mol of phenol, thus insuring a major proportion of dialkylation with the heavier reactant. It is thus possible to obtain up to about 50% to 75% of the reaction product comprised of phenolic molecules having dialkylation with octyl or nonyl groups and

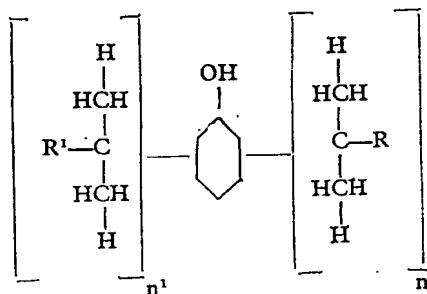
monoalkylation with butyl or amyl groups. The remaining reaction products will be various proportions and combinations of other di- and tri-tertiary alkyl phenols with alkylation in the para and ortho positions, almost no alkylation occurring in the meta positions. An excess of tertiary butylene or amylene in the second step tends to promote complete reaction to the trisubstituted compounds.

The preferred antioxidant composition of this invention is a mixture of tertiary alkylated phenols which have the structural formula



wherein x is an integer ranging from 2 to 3, n is an integer ranging from 0 to 3 but not exceeding the value of x, wherein R is selected from the group consisting of tertiary butyl and tertiary amyl and R¹ is selected from the group consisting of tertiary octyl and tertiary nonyl, R and R¹ being attached to the benzene ring in the 2, 4 and 6 positions with respect to the hydroxyl group, and wherein a major proportion of said mixture is comprised of tri-tertiary-alkylated phenols wherein two of said tertiary alkyl radicals are selected from the group consisting of tertiary octyl and tertiary nonyl radicals and wherein the third tertiary alkyl radical is selected from the group consisting of tertiary butyl and tertiary amyl radicals.

The reaction product can also be described as a mixture of phenols having the structural formula



wherein n and n' are integers ranging from 1 to 2, but not totalling more than 3, wherein R is a monovalent radical selected from the group consisting of CH₃ and C₂H₅ and R' is selected from the group consisting of C₂H₅, C₃H₇ and C₄H₉, wherein alkylation of the phenolic ring is in the 2, 4 and 6 positions, and wherein a major proportion of said mixture is comprised of tri-tertiary-alkylated phenols wherein two of said tertiary alkyl

radicals are selected from the group consisting of tertiary octyl and tertiary nonyl radicals and the third tertiary alkyl radical is selected from the group consisting of tertiary butyl and tertiary amyl radicals.

The preparation of the products of the invention is illustrated by following examples:

EXAMPLE 1.

Phenol, diisobutylene and isobutylene were reacted in the presence of sulfuric acid in the molar ratio of 1:2:1 to provide a reaction product of mixed tertiary octyl, tertiary butyl phenols. Three hundred seventy-six grams of phenol and 32 grams of concentrated sulfuric acid were warmed to 70° C. and then 896 grams of diisobutylene were added over a period of 3 hours, the temperature being maintained at about 70° C. to 80° C. After further stirring for about 1 hour, 224 grams of isobutylene were added to the reaction mixture to complete the alkylation. Finally the catalyst was neutralized with aqueous sodium carbonate and volatile materials were removed by distillation under vacuum. Suspended material was then removed by filtration. This yielded about 80% of the theoretical amount of reaction product, based on the weight of the reactants.

EXAMPLE 2.

Phenol, diisobutylene and isobutylene were reacted in the presence of sulfuric acid in the molar ratio of 1:1:2 to provide a reaction product of mixed tertiary octyl, tertiary butyl phenol. Two hundred eighty-two grams of phenol and 12 grams of concentrated sulfuric acid were heated to about 70° C. Thereafter, 336 grams of diisobutylene were added. The temperature was maintained between 70° C. and 80° C. for about two hours while the mixture was being stirred. Three hundred thirty-six grams of isobutylene were then added, the temperature being maintained within the same range for about $\frac{1}{2}$ hour. The excess sulfuric acid was neutralized and the reaction product obtained as in Example 1. The resultant reaction product contained about 910 grams of mixed tertiary octyl, tertiary butyl phenol.

EXAMPLE 3.

Phenol, diisobutylene and isobutylene were reacted in the molar ratio of 1:1.5:1.5 in the presence of a sulfuric acid catalyst. Two hundred eighty-two grams of phenol and 12 grams of concentrated sulfuric acid were heated together to about 70° C. to 80° C. Thereafter, 504 grams of diisobutylene were added and the mixture was maintained between 70° C. and 80° C. for about two hours. Two hundred fifty-two grams of isobutylene were then added while the temperature was maintained within a range of 70° C. to 80° C. The catalyst was destroyed and the reaction products obtained as in the above

examples, yielding 928 grams of reaction product.

EXAMPLE 4.

Phenol, diisobutylene and isobutylene were reacted in the molar ratio of 1:1.25:1.75 as in the above examples except that 420 grams of diisobutylene and 294 grams of isobutylene were used to react with 282 grams of phenol. The reaction product weighed 896 grams.

In the practice of the invention, it is often desirable to use an excess of certain reactants in order to insure desired complete alkylation of the phenolic ring in the ortho and para positions. Examples 5 and 6 below illustrate this practice:

EXAMPLE 5.

Phenol, diisobutylene and isobutylene were reacted in the molar ratio of 1:2:1.25 so that an excess of isobutylene was present during the second reaction step. Two hundred eighty-two grams of phenol, 672 grams of diisobutylene and 210 grams of isobutylene were reacted according to the method shown in Example 1. After removal of the catalyst and the unreacted components, 973 grams of reaction product were obtained.

EXAMPLE 6.

Following the procedure of Example 1, phenol, diisobutylene and isobutylene were reacted in a molar ratio of 1:2:1.5 so that an excess of isobutylene was present during the second alkylation step. This was accomplished by reacting 672 grams of diisobutylene with 282 grams of phenol and then reacting that product with 252 grams of isobutylene. This gave a reaction product weighing 1005 grams.

The invention is further illustrated by the following examples:

EXAMPLE 7.

Phenol, tripropylene and isobutylene were reacted in stepwise fashion in the presence of a catalyst in the molar ratio of 1:1:2. Ninety-four grams of phenol and 8 grams of concentrated sulfuric acid were heated to about 125° C. While maintaining the temperature between 125° C. and 140° C., 126 grams of tripropylene were added. The mixture was maintained within the indicated temperature range and stirred for about two hours. Thereafter, 112 grams of isobutylene were added in order to complete the alkylation. After the temperature had been reduced to about 70° C. to 80° C. the catalyst was destroyed and the reaction product was isolated as indicated in the above examples, yielding a reaction product weighing 246 grams.

EXAMPLE 8.

Para-tertiary-nonyl phenol and isobutylene were reacted in the molar ratio of 1:2. Two hundred twenty grams of para-tertiary-nonyl phenol and 4 grams of concentrated sulfuric acid were heated to about 70° C. Thereafter, 112 grams of isobutylene were added while

the temperature was maintained within a range of 80° C. to 100° C. for about two hours. This procedure gave a substantially trialkylated product. Thereafter, the catalyst was destroyed by neutralizing with aqueous sodium carbonate and the reaction product was obtained as in Example 1, yielding 305 grams.

EXAMPLE 9.

Phenol, diisobutylene and 2-methylbutene-1 were reacted in a molar ratio of 1:2:1. The same procedure as used in Example 1 was used except that 448 grams of diisobutylene and 142 grams of 2-methylbutene-1 were reacted with 188 grams of phenol. After removal of the catalyst, unreacted materials, and by-products, 605 grams of reaction product remained.

EXAMPLE 10.

Para-tertiary-nonyl phenol and 2-methylbutene-1 were reacted in the molar ratio of 1:2. One hundred ten grams of parateriary-nonyl phenol and 2 grams of concentrated sulfuric acid were heated at about 70° C. Thereafter, 71 grams of 2-methylbutene-1 were added while maintaining the temperature between 70° C. and 80° C. This mixture was stirred for about one hour before removing the catalyst and unreacted materials as indicated in previous examples. The reaction product weighed 164 grams.

This invention is primarily concerned with phenolic reaction products and the process of preparing them because they represent superior antioxidants, and are much cheaper to prepare than pure compounds. However, pure compounds can be made and are also superior antioxidants.

The following examples represent the preparation of pure tertiary octyl, tertiary butyl phenols wherein the position para to the hydroxyl is occupied by a tertiary octyl group.

EXAMPLE 11.

2,4-Di-tertiary-octyl-6-tertiary-butyl phenol was prepared as follows. 2,4-Di-tertiary octyl phenol was separated from a mixture of di-octyl phenols which was prepared by reacting phenol with diisobutylene. Two hundred twenty-two and six-tenths grams of the isolated compound were dissolved in 150 milliliters of toluene. Thereafter, 4.0 grams of concentrated sulfuric acid were added and the mixture was warmed to 50° C. Isobutylene was then added until no further absorption took place. The catalyst was then destroyed and the 2,4-di-tertiary-octyl-6-tertiary-butyl phenol was separated by distillation under vacuum. Two hundred twenty-four and five-tenths grams of pure compound were obtained between 153 and 156° C. at 4 mm. of pressure. After recrystallization from ethanol by cooling in an ice bath, the product had a melting point of 50—51° C. Analysis for carbon and hydrogen gave 82.85% carbon,

and 12.26% hydrogen, which compares with the theoretical calculation of 83.35% carbon and 12.30% hydrogen.

EXAMPLE 12.

5 2,6-Di-tertiary-butyl-4-tertiary-octyl phenol was prepared as follows: two hundred six grams of pure para-tertiary-octyl phenol were dissolved in 200 milliliters of toluene and then mixed with 3 grams of concentrated
10 sulfuric acid. This mixture was warmed to 50° C. and then 110 grams of isobutylene were added during a period of three and a half hours. The catalyst was destroyed and the product was then separated by distillation
15 within a temperature range of 181° C. and 187° C. at 20 mm. of pressure. This provided 240 grams of 2,6-di-tertiary-butyl-4-tertiary-octyl phenol. After recrystallization from ethanol, this product had a melting
20 point of 45–46° C. Analysis for carbon and hydrogen gave 82.72% carbon and 12.02% hydrogen, which compares with a theoretical

calculation of 83.0% carbon and 11.95% hydrogen.

The efficacy of the products of this invention as antioxidants or age resistors for natural and synthetic rubbers and rubber-like materials is illustrated by the following described tests. 25

Various products of the invention were compounded in the following formula: 30

	Parts by weight	
Extracted pale crepe	100.0	
Zinc oxide	5.0	35
Sulfur	3.0	
Hexamethylene tetramine	1.0	
Stearic acid	1.5	
Antioxidant	1.0	

Test samples were vulcanized for 50 minutes at 285° F., giving the results indicated in Table I. 40

TABLE I.

Antioxidant	Tensile		% T.R.	% Wt. Incr.
	Orig.	Final	18 days O ₂ bomb	18 days O ₂ bomb
Control—No A.O.	2000	0	0	18.0
Antioxidant A	1850	575	33.8	1.21
R.P. Phenol-diisobutylene-				
isobutylene				
1:2:1	1750	1350	75.0	0.38
1:1:2	1800	1200	66.7	0.32
1:1.25:1.75	1850	1550	83.8	0.39
1:1.5:1.5	1900	1450	76.3	0.34
1:1.75:1.25	1850	1300	70.3	0.35
1:1.5:1.75	1800	1500	83.3	0.42
1:2:1.25	2075	1300	62.7	0.42
1:2:1.5	1950	1400	71.8	0.34
1:2:0	1625	750	46.2	0.59
2,4-Di-tertiary-octyl-6-tertiary-				
butyl phenol	2050	1500	73.2	0.64
2,6-Di-tertiary-butyl-4-tertiary-				
octyl phenol	1800	1450	80.6	0.32
R.P. Nonyl phenol-isobutylene				
1:2	1675	1350	81.0	0.23
R.P. Phenol-tripropylene-				
isobutylene				
1:1:2	1800	1100	61.0	0.26

Note 1—"Antioxidant A" is a commercial nonstaining antioxidant comprising a mixture of alkylated phenols.

Note 2—"R.P." means "reaction product."

Note 3—"T.R." means "tensile retention."

When the products of the invention were compounded in a white rubber formulation containing natural rubber, sulfur, zinc oxide, calcium carbonate, stearic acid and antioxidant in the relationship of 1 part antioxidant to 100 parts natural rubber and were exposed in a weatherometer for 48 hours, they compared favorably with commercial non-staining antioxidants.

Use of the term "a rubber" is intended to include natural rubber and the various synthetic rubbers and rubber-like materials which are similar from the standpoint of aging, e.g. polychloroprene, the rubbery copolymerization products of a major proportion of a monoolefin (such as isobutylene) and a minor proportion of a multi-olefin (such as butadiene or isoprene), the rubbery copolymers of butadiene and styrene, and the rubbery copolymers of butadiene and acrylonitrile.

The term "tertiary alkyl" is intended to denote alkyl radicals which are attached to the aromatic ring through a tertiary carbon atom.

The products of this invention are useful as antioxidants or age resistors for vulcanized or unvulcanized rubbers in various forms, including latex.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the scope of the invention, as defined in the appended claims.

What we claim is:—

1. A process for the preparation of substantially trialkylated phenols which includes the steps of first reacting phenol with one or more tertiary octenes and/or tertiary nonenes, then reacting the alkylated product of the first step with isobutylene and/or a tertiary pentene.

2. A process according to Claim 1 in which one mol of phenol is reacted with at least one mol of olefin in the first step, then said reaction product being reacted with at least 1 mol of another olefin, the total amount of olefin used being at least three mols per mol of phenol.

3. A process according to Claim 2 which includes the presence of an acid catalyst in the first stage reaction, conducting this reaction at a temperature from 50° to 150° C., the second stage reaction being carried out at a temperature less than 90° C.

4. A process according to Claim 3 in which a major portion of the alkyl radicals in the reaction product is represented by tertiary octyl and/or tertiary nonyl radicals.

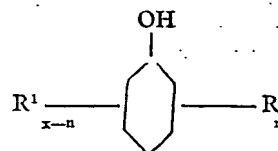
5. A process according to Claim 3 in which the first stage olefin reactant is a diisobutylene, and the second stage olefin reactant is

isobutylene.

6. A trialkylated reaction product which includes the reaction product of phenol and two tertiary olefins, one of said olefins being a tertiary octene or a tertiary nonene and the other olefin being isobutylene or a tertiary pentene, the first-mentioned olefin predominating.

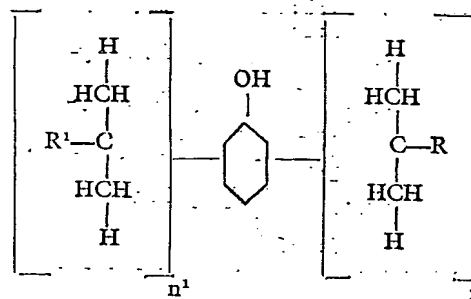
7. A trialkylated reaction product resulting from the reaction of phenol, diisobutylene and isobutylene, in which the amount of diisobutylene exceeds the amount of isobutylene.

8. A mixture of tertiary alkylated phenols which have the structural formula



wherein x is selected from the group consisting of 2 and 3, and n is selected from the group consisting of 0, 1, 2, and 3 but not exceeding the value of x, and wherein R is selected from the group consisting of tertiary butyl and tertiary amyl radicals and R¹ is selected from the group consisting of tertiary octyl and tertiary nonyl radicals, R and R¹ being attached to the benzene ring in the 2,4 and 6 positions, and wherein a major proportion of said mixture is comprised of tri-tertiary-alkylated phenols wherein two of said tertiary alkyl radicals are selected from the group consisting of tertiary octyl and tertiary nonyl radicals and wherein the third tertiary alkyl radical is selected from the group consisting of tertiary butyl and tertiary amyl radicals.

9. A mixture of tertiary alkylated phenols which have the structural formula



wherein n and n¹ are selected from the group consisting of 1 and 2, but not totalling more than 3, wherein R is selected from the group consisting of CH₃ and C₂H₅ and R¹ is selected from the group consisting of C₆H₁₁ and C₆H₁₃, wherein alkylation of the phenolic ring is in the 2,4 and 6 positions, and wherein a major proportion of said mixture is com-

- 5 prised of tri - tertiary - alkylated phenols wherein two of said tertiary alkyl radicals are selected from the group consisting of tertiary octyl and tertiary nonyl radicals and the third tertiary alkyl radical is selected from the group consisting of tertiary butyl and tertiary amyl radicals.
- 10 10. A mixture consisting chiefly of mono hydroxy benzenes having only tertiary octyl and tertiary butyl substituents, there being present on each benzene ring at least one tertiary octyl and at least one tertiary butyl substituent and the total number of alkyl substituents being not less than three.
- 15 11. As a new composition, 2,4-ditertiary-octyl-6-tertiary-butyl phenol.
- 20 12. A method of preserving a rubber which includes treating the rubber with a mixture of tertiary alkylated phenols as set forth in claim 8.
13. A method of preserving a rubber which includes treating the rubber with a mixture of tertiary alkylated phenols as set forth in claim 9.
14. A rubber product which has been treated with a mixture of tertiary alkylated phenols as set forth in claim 8.
15. A rubber product which has been treated with a mixture of tertiary alkylated phenols as set forth in claim 9.
16. A process for the preparation of alkylated phenols substantially as set forth and described hereinbefore.
17. An alkylated reaction product substantially as set forth and described hereinbefore.
18. A mixture of tertiary alkylated phenols substantially as set forth and described hereinbefore.
19. A method of preserving a rubber substantially as set forth and described hereinbefore.
20. A rubber product substantially as set forth and described hereinbefore.
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